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CERTIFICATION

This is to certify that

(1) I am a German into English and English into German translator, accredited by the American Translators Association;

(2) I have translated the following document(s):

WO 99/04750, "Use Of Polymers Containing Polysiloxane forCosmetic Formulations"

from German to English.

(3) The attached English translation is a true and correct translation of the German source document to the best of my knowledge and belief.

Date: Aug 7, 2001

Ruth Boggs, M.A.

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(54) **Title:** USE OF POLYMERS CONTAINING POLYSILOXANE FOR COSMETIC FORMULATIONS

(57) **Abstract**

The invention relates to a method for producing polymers which are water-soluble or water-dispersible or which, if they consist of monomers with neutralizable radicals, are water-soluble or water-dispersible in the neutralized form, by radically polymerizing a) ethylenically unsaturated monomers in the presence of b) silicone derivatives containing polyalkyleneoxide.

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Use of Polymers Containing Polysiloxane for Cosmetic Formulations

Description

For almost 50 years, synthetic polymers have been used successfully for setting hairstyles. At first, vinyl lactam homopolymers and copolymers were preferred, but subsequently polymers containing carboxylate groups have become increasingly important. The desired profile of properties such as a strong setting effect in the presence of high atmospheric humidity, elasticity, ability to be washed out of the hair and compatibility with the other ingredients of the formulation are achieved by copolymerization of a combination of hydrophobic monomers, elasticizing monomers and monomers that contain carboxyl groups.

The requirements mentioned above are met today by various types of polymers, but the feel of hairstyles set using these polymers is often perceived as unpleasantly dull and "unnatural." Attempts to improve these formulations by means of additives have not yet led to fully satisfactory results. Although the addition of conventional plasticizers improves the feel, in many cases it also at the same time reduces the hold. The commonly used polysiloxanes are not compatible with polar polymers and often require other additives to allow them to be formulated at all. Separation during storage of the formulation and even during use can lead to problems.

Therefore, there has been no lack of attempts to bind polysiloxane groups to the hair setting polymer by covalent bonds to prevent separation. For example, European Patent Application 0408311 describes hair care polymers consisting of a monomer containing polysiloxane groups plus the conventional hydrophilic and hydrophobic monomers. European Patent Applications 0412704 through 0412707 propose that polysiloxane groups in the form of macromonomers with a molecular weight of 1,000 to 50,000 be polymerized with the conventional hydrophobic and hydrophilic monomers. However, synthesis of these monomers is extremely complicated. It is difficult to separate unreacted macromonomers and their unreactive impurities from these polymers because of their high molecular weight. They are a toxicological and allergenic risk. In addition, in order to achieve a good effect, the resulting copolymers can often be formulated only in combination with other polymers, carriers and other additives as instructed in the aforementioned patents.

German Patent 42 40 108 describes bonding agents that contain polysiloxane and are suitable as dirt-repellant coatings, in particular as anti-graffiti coatings. However, these bonding agents contain lacquer

and are not suitable for cosmetic purposes.

German Patent 16 45 569 describes a method of producing organosilicon graft copolymers and their use as foam compositions.

The object of this invention is to provide polymers for hair care products without the disadvantages described above.

It has been discovered that polymers that are water-soluble or water-dispersible in water or, in the case when they consist of monomers with neutralizable groups, they are water-soluble or water-dispersible in a neutralized form, can be used for cosmetic formulations, with said polymers being accessible by radical polymerization of

(a) ethylenically unsaturated monomers in the presence of
(b) silicone derivatives containing polyalkylene oxide.

The term "water dispersible" in the sense of this invention is understood to refer to polymers which, within 24 hours after coming in contact with water, form a fluid that does not contain any solid particles visible to the naked eye without the aid of optical devices. To determine whether a polymer is water dispersible, 100 mg of the polymer in the form of a film 100 µm thick is placed in 100 mL water (20 °Celsius) and agitated for 24 hours on a conventional agitated stand. If no solid particles can be detected after agitation, but the fluid is cloudy, the polymer is water dispersible. If there is no cloudiness, the polymer is considered water-soluble.

If the silicone compounds are not present during polymerization but instead are added after polymerization, very soft sticky films, which are not suitable for the applications in hair care products according to this invention, are usually obtained (see Comparative Examples 8 and 24).

This indicates that grafting of the polymers onto the silicone compounds may occur during polymerization, contributing to the good film properties such as not being sticky, high surface smoothness and hardness. However, mechanisms other than grafting are also conceivable for imparting advantageous properties to the polymers according to this invention.

Ethylenically unsaturated monomers are preferably used as suitable polymerizable monomers (a). Either a single monomer or a combination of two or more monomers may be used. The term polymerizable is understood to mean that the monomers that are used can be polymerized by using any

conventional method of synthesis.

For example, such methods may include solution polymerization, emulsion polymerization, inverse polymerization, suspension polymerization or inverse suspension polymerization or precipitation polymerization, although the methods that can be used are not limited to these. In solution polymerization, water, conventional organic solvents or the silicone derivatives according to this invention themselves may be used as the solvents.

Monomers that can be polymerized with a reaction initiated by free radicals are preferred. The term ethylenically unsaturated means that the monomers have at least one polymerizable carbon-carbon bond which may be mono-, di-, tri- or tetra-substituted.

The monomers (a) of the polymers containing polysiloxane according to the present invention may constitute 50 to 99.9 percent by weight, preferably 70 to 99 percent by weight, and especially 85 to 98 percent by weight.

The preferred ethylenically unsaturated monomers (a) can be described by the following general formula:

$$X\text{-}C(O)CR^7{=}CHR^6$$

where

X is selected from the group consisting of -OH, -OM, $-OR^8$, NH_2, $-NHR^8$, $X(R^8)_2$,

M is a cation selected from the group consisting of Na^+, K^+, Mg^{++}, Ca^{++}, Zn^{++}, NH_4^+, alkylammonium, dialkylammonium, trialkylammonium and tetraalkylammonium;

the R^8 groups may be identical or different and are selected from the group consisting of -H, C_1 to C_{40} linear or branched alkyl groups, N,N-dimethylaminoethyl, 2-hydroxyethyl, 2-methoxyethyl, 2-ethoxyethyl, hydroxypropyl, methoxypropyl or ethoxypropyl.

R^7 and R^6 are selected independently of one another from the group consisting of -H, C_1 to C_8 linear or branched alkyl chains, methoxy, ethoxy, 2-hydroxyethoxy, 2-methoxyethoxy and 2-ethoxyethyl.

Representative but not limiting examples of suitable monomers (a) include acrylic acid and its salts, esters and amides, for example. The salts may be derived from any desired nontoxic metal, ammonium or substituted ammonium counterion.

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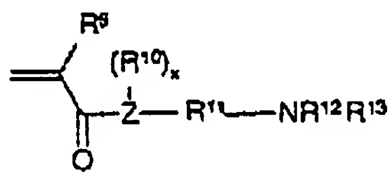
The esters may be derived from C_1 to C_{12} linear alcohols, C_3 to C_{40} branched alcohols or C_3 to C_{40} carbocyclic alcohols, polyfunctional alcohols with 2 to approximately 8 hydroxyl groups such as ethylene glycol, hexylene glycol, glycerol and 1,2,6-hexanetriol or they may be derived from amino alcohols or alcohol ethers such as methoxyethanol and ethoxyethanol or polyethylene glycols.

Also suitable are N,N-dialkyl aminoalkyl acrylates and methacrylates and N-dialkyl aminoalkyl acrylamides and methacrylamides of general formula



(II)

where R^9	= H, alkyl with 1 to 8 carbons,
R^{10}	= H, methyl
R^{11}	= alkylene with 1 to 24 carbons, optionally with an alkyl substituent,
R^{12}, R^{13}	= C_1 to C_{40} alkyl group,
z	= nitrogen when x = 1 or oxygen when x = 0

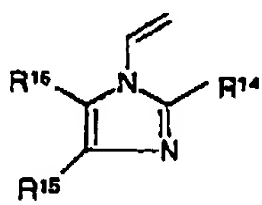
The amides may be unsubstituted, N-alkyl-mono-substituted or N-alkylamino-mono-substituted or N,N-dialkyl-substituted or N,N-dialkylamino-disubstituted, where the alkyl or alkylamino groups are derived from C_1 to C_{40} linear units, C_3 to C_{40} branched units or C_3 or C_{40} carbocyclic units. In addition, the aminoalkyl groups may also be quaternized.

Preferred monomers of formula II include N,N-dimethylaminomethyl (meth)acrylate, N,N-diethylaminomethyl(meth)acrylate, N,N-dimethylaminoethyl(meth)acrylate, N,N-diethylaminoethyl(meth)acrylate.

Monomers (a) that can also be used include substituted acrylic acids as well as the salts, esters and amides thereof, where the substituents on the carbon atoms are in position 2 or 3 of acrylic acid and are selected independently of one another from the group consisting of C_1 to C_4 alkyl, -CN, COOH, especially preferably methacrylic acid, ethacrylic acid and 3-cyanoacrylic acid. These salts, esters and amides of these substituted acrylic acids may be selected as described above for the salts, esters and amides of acrylic acid.

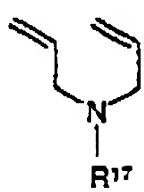
Other suitable monomers (a) include the vinyl and allyl esters of C_1 to C_{40} linear carboxylic acids, C_3 to C_{40} branched carboxylic acids or C_3 to C_{40} carbocyclic carboxylic acids (e.g., vinyl acetate, vinyl propionate, vinyl neononanoate, vinyl neoundecanoic acid or tert-butylbenzoic acid vinyl ester); vinyl halides or allyl halides, preferably vinyl chloride and allyl chloride, vinyl ethers, preferably methyl, ethyl, butyl or dodecyl vinyl ether, vinylformamide, vinylmethylacetamide, vinylamine; vinyllactams, preferably vinylpyrrolidone and vinylcaprolactam, vinyl-substituted or allyl-substituted heterocyclic compounds, preferably vinylpyridine, vinyloxazoline and allylpyridine.

In addition, N-vinylimidazoles of general formula III are also suitable, where R^{14} through R^{16} independently of one another stand for hydrogen, C_1 to C_4 alkyl or phenyl:



(III)

Other suitable monomers (a) include diallylamines of general formula (IV)



(IV)

where R^{17} = C_1 to C_{24} alkyl.

Other suitable monomers (a) include vinylidene chloride and hydrocarbons having at least one carbon-carbon double bond, preferably styrene, alpha-methylstyrene, tert-butylstyrene, butadiene, isoprene, cyclohexadiene, ethylene, propylene, 1-butene, 2-butene, isobutylene, vinyltoluene and mixtures of these monomers.

Especially suitable monomers (a) include acrylic acid, methacrylic acid, ethyl acrylic acid, methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, tert-butyl acrylate, 2-ethylhexyl

acrylate, decyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, 2-ethylhexyl methacrylate, decyl methacrylate, methyl ethacrylate, ethyl ethacrylate, n-butyl ethacrylate, isobutyl ethacrylate, tert-butyl ethacrylate, 2-ethylhexyl ethacrylate, decyl ethacrylate, 2,3-dihydroxypropyl acrylate, 2,3-dihydroxypropyl methacrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl ethacrylate, 2-methoxyethyl acrylate, 2-methoxyethyl methacrylate, 2-methoxyethyl ethacrylate, 2-ethoxyethyl methacrylate, 2-ethoxyethyl ethacrylate, hydroxypropyl methacrylate, glyceryl monoacrylate, glyceryl monomethacrylate, polyalkylene glycol (meth)acrylates, unsaturated sulfonic acids such as acrylamidopropanesulfonic acid;

acrylamide, methacrylamide, ethacrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-ethylacrylamide, N-isopropylacrylamide, N-butylacrylamide, N-tert-butylacrylamide, N-octylacrylamide, N-tert-octylacrylamide, N-octadecylacrylamide, N-phenylacrylamide, N-methylmethacrylamide N-ethylmethacrylamide, N-dodecylmethacrylamide, 1-vinylimidazole, 1-vinyl-2-methylimidazole, N,N-dimethylaminomethyl (meth)acrylate, N,N-diethylaminomethyl (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N,N-dimethylaminobutyl (meth)acrylate, N,N-diethylaminobutyl (meth)acrylate, N,N-dimethylaminohexyl (meth)acrylate, N,N-dimethylaminooctyl (meth)acrylate, N,N-dimethylaminododecyl (meth)acrylate, N-[3-(dimethylamino)propyl]methacrylamide, N-[3-(dimethylamino)propyl]acrylamide, N-[3-(dimethylamino)butyl]methacrylamide, N-[8-(dimethylamino)octyl]methacrylamide, N-[12-dimethylamino)dodecyl]methacrylamide, N-[3-(diethylamino)propyl]methacrylamide, N-[3-(diethylamino)propyl]acrylamide;

maleic acid, fumaric acid, maleic anhydride and its semiesters, crotonic acid, itaconic acid, diallyldimethylammonium chloride, vinyl ethers (such as methyl, ethyl, butyl or dodecylvinyl ether), vinylformamide, vinylmethylacetamide, vinylamine; vinyl methyl ketone, maleimide, vinylpyridine, vinylimidazole, vinylfuran, styrene, styrene sulfonate, allyl alcohol and mixtures thereof.

Of these, compounds that are especially preferred include acrylic acid, methacrylic acid, maleic acid, fumaric acid, crotonic acid, maleic anhydride and its semiesters, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, n-butyl methacrylate, tert-butyl acrylate, tert-butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, 2-ethylhexyl acrylate, N-tert-butyl

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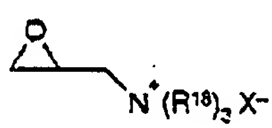
acrylamide, N-octylacrylamide, 2-hydroxyethyl acrylate, hydroxypropyl acrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate, alkylene glycol (meth)acrylate, unsaturated sulfonic acids and, for example, acrylamidopropanesulfonic acid, vinylpyrrolidone, vinylcaprolactam, vinyl ethers (such as methyl, ethyl or dodecylvinyl ether), vinylformamide, vinylmethylacetamide, vinylamine, 1-vinylimidazole, 1-vinyl-2-methylimidazole, N,N-dimethylaminomethyl methacrylate and N-[3-(dimethylamino)propyl]methacrylamide; 3-methyl-1-vinylimidazolium chloride, 3-methyl-1-vinylimidazolium ethyl sulfate, N,N-dimethylaminoethyl methacrylate, N-[3-(dimethylamino)propyl]methacrylamide, quarternized with methyl chloride, methyl sulfate or diethyl sulfate.

Monomers having a basic nitrogen atom can be quaternized by the following method.

For example, alkyl halides with 1 to 24 carbon atoms in the alkyl group, such as methyl chloride, methyl bromide, methyl iodide, ethyl iodide, ethyl bromide, propyl chloride, hexyl chloride, dodecyl chloride, lauryl chloride and benzyl halides, in particular benzyl chloride and benzyl bromide, are suitable for quaternization of the amines. Other suitable quaternizing agents include dialkyl sulfates, in particular dimethyl sulfate or diethyl sulfate. Quaternization of the basic amines can also be performed with alkylene oxides such as ethylene oxide or propylene oxide in the presence of acids. Preferred quaternizing agents include methyl chloride, dimethyl sulfate or diethyl sulfate.

This quaternization may be performed before or after polymerization.

In addition, the reaction products of unsaturated acids such as acrylic acid or methacrylic acid with a quaternized epichlorohydrin of general formula (V) may also be used (R^{10} = C_1 to C_{40} alkyl).



(V)

Examples include (meth)acryloyloxyhydroxypropyl trimethylammonium chloride and (meth)acryloyloxyhydroxypropyl triethylammonium chloride.

The basic monomers may also be cationized by neutralizing them with mineral acids such as sulfuric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, phosphoric acid or nitric acid or with organic acids such as formic acid, acetic acid, lactic acid or citric acid.

In addition to the monomers mentioned above, so-called macromonomers may also be used as monomers (a), such as macromonomers containing silicone and having one or more radically polymerizable groups or alkyloxazoline macromonomers such as those described in European Patent 408 311, for example.

In addition, monomers containing fluorines such as those described in European Patent 558423 or compounds which have a crosslinking action or which regulate the molecular weight may also be used either in combination or alone.

Molecular weight regulators which may also be used include the usual compounds, with which those skilled in the art are familiar, such as sulfur compounds (e.g., mercaptoethanol, 2-ethylhexyl thioglycolate, thioglycolic acid or dodecylmercaptan), as well as tribromochloromethane or other compounds which have a regulating effect on the molecular weight of the resulting polymers.

Optionally silicone compounds containing thiol groups may also be used. Silicone-free regulators are preferred.

Compounds having at least two ethylenically unsaturated double bonds such as the esters of ethylenically unsaturated carboxylic acids, e.g., acrylic acid or methacrylic acid and polyhydric alcohols, ethers of at least dihydric alcohols such as vinyl ethers or allyl ethers may also be used as the crosslinking monomers. Straight-chain or branched, linear or cyclic aliphatic or aromatic hydrocarbons having at least two double bonds which may not be conjugated in the case of aliphatic hydrocarbons are also suitable. Furthermore, amides of acrylic acid and methacrylic acid and N-allylamines of at least divalent amines (e.g., 1,2-diaminoethane, 1,3-diaminopropane) are also suitable. Furthermore, triallylamine or the corresponding ammonium salts, N-vinyl compounds of urea derivatives, at least divalent amides, cyanurates or urethanes are also suitable. Other suitable crosslinking agents include divinyldioxane, tetraallylsilane or tetravinylsilane.

Especially preferred crosslinking agents include, for example, methylene bisacrylamide, triallylamine and triallylammonium salts, divinylimidazole, N,N'-divinylethylene urea, conversion products of polyhydric alcohols with acrylic acid or methacrylic acid, methacrylic acid esters and acrylic acid esters of polyalkylene oxides or polyhydric alcohols which have been reacted with ethylene oxide and/or propylene oxide and/or epichlorohydrin.

Other polymers such as polyamides, polyurethanes, polyesters, homopolymers and copolymers of ethylenically unsaturated monomers may

optionally also be present during polymerization of monomers (a). Examples of such polymers, some of which are also used in cosmetics, include the polymers known by the brand names Amerhold™, Ultrahold™, Ultrahold Strong™, Luviflex™, VBM, Luvimer™, Acronal™, Acudyne™, Stepanhold™, Lovocryl™, Versatyl™, Amphomer™ or Eastma AQ™.

Such polymers and others may also be added to the polymer preparations according to this invention after polymerization.

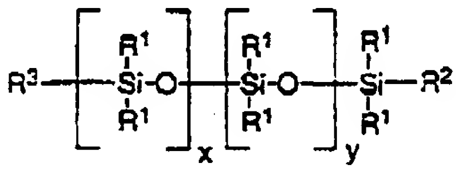
Monomers A according to this invention, if they contain ionizable groups, may be neutralized completely or in part with acids or bases before or after polymerization to thus adjust the water solubility or water dispersibility to the desired extent.
Mineral bases such as sodium carbonate, alkali hydroxides and ammonia, organic bases such as amino alcohols, specifically 2-amino-2-methyl-1-propanol, monoethanolamine, diethanolamine, triethanolamine, triisopropylamine, tri[(2-hydroxyl)-1-propyl]amine, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-hydroxymethyl-1,3-propanediol and diamines such as lysine may also be used as neutralizing agents for monomers having acid groups.
Suitable neutralizing agents for monomers having cationizable groups include mineral acids such as hydrochloric acid, sulfuric acid or phosphoric acid as well as organic acids such as carboxylic acid, lactic acid, citric acid or others.

In addition, such additives as plasticizers, film-forming aids, pigments, perfumes or other additives may also be added, either alone or in combination, during polymerization and/or after polymerization.

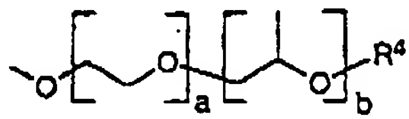
For use of the polymers according to this invention in hair care products, especially for use as hair setting products, it is advantageous to adjust the glass transition temperature of the polymer products to a level of more than 20 °Celsius through a suitable combination of ethylenically unsaturated monomers.

Suitable silicone derivatives (b) include the compounds known by the INCI names dimethicone copolyols or silicone surfactants such as those available under the brand names Abil® (from T. Goldschmidt), Alkasil® (Rhone Poulenc), Silicone Polyol Copolymer® (Genesse), Belsil® (Wacker), Silwat® (Witco, Greenwich, CT, USA) or Dow Corning (from Dow Corning). These products contain compounds having the CAS numbers 64365-23-7, 68937-54-2, 68938-54-5, 68937-55-3.

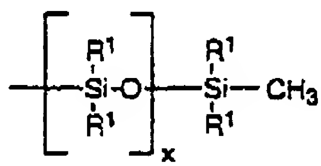
Especially suitable monomers (b) include those containing the following structural elements:


(1)

where:

R^2 = CH_3 oder 

R^3 = CH_3 oder R^2

R^4 = H, CH_3, 

[Translator's note: "oder" = "or"]

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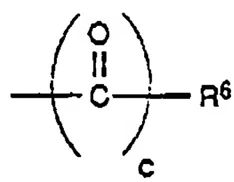
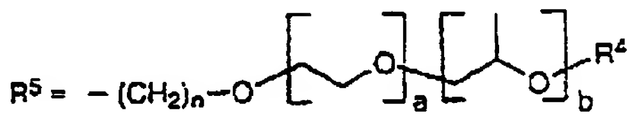


R^6 is an organic group consisting of 1 to 40 carbon atoms which may contain amino groups, carboxylic acid groups or sulfonate groups, or in the case when c = 0, it may also be the anion of an inorganic acid,

and where the R^1 groups may be the same or different and are selected either from the group of aliphatic hydrocarbons with 1 to 20 carbon atoms, cyclic aliphatic hydrocarbons with 3 to 20 carbon atoms, or they may be of an aromatic type, or they may be the same as R_5 [sic; R^5] where:



with the provision that at least one of the R^1, R^2 or R^3 groups is a group containing a polyalkylene oxide group according to the definition given above,
and n is an integer from 1 to 6,
x and y are integers such that the molecular weight of the polysiloxane block is between 300 and 30,000,
a and b are integers between 0 and 50, with the provision that the sum of a + b is greater than 0 and c is 0 or 1.

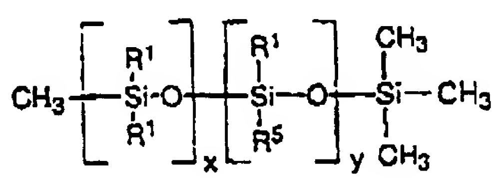
Preferred R^2 and R^5 groups include those in which the sum of a + b is between 5 and 30.

The R^1 groups are preferably selected from the following group: methyl, ethyl, propyl, butyl, isobutyl, pentyl, isopentyl, hexyl, ocytl, decyl, dodecyl and octadecyl, cycloaliphatic groups, specifically cyclohexyl, aromatic groups, specifically phenyl or naphthyl, mixed aromatic-aliphatic groups such as benzyl or phenylethyl and tolyl and xylyl as well as R^5.

Especially suitable R^4 groups are those in which, in the case where $R^4 = -(CO)_c-R^6$, R^6 is any desired alkyl group, cycloalkyl group or aryl group which has between 1 and 40 carbon atoms and which may also have additional ionic groups such as NH_2, COOH, SO_3H.

Preferred inorganic R^6 groups are phosphate and sulfate for the case when c = 0.

Especially preferred silicone derivatives (b) are those having the following general structure:



The silicone derivatives (b) are usually present in amounts of 0.1 to 50 percent by weight, preferably 1 to 20 percent by weight and especially 2

to 15 percent by weight, in the polymer products according to this invention.

Especially suitable polymers are those which are water soluble or whose water dispersibility is so great that they are soluble in an amount of more than 0.1 g/L, preferably more than 0.2 g/L, in a 50:50 water/ethanol solvent mixture (vol%:vol%).

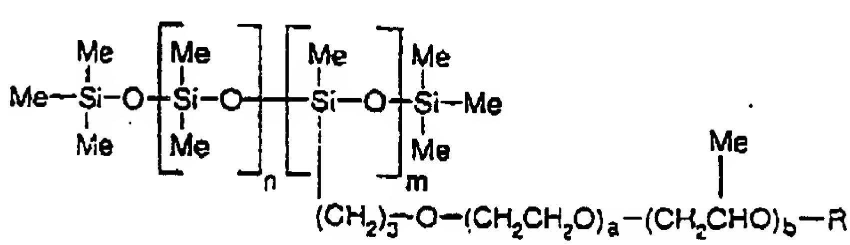
For the case when the polymers consist of monomers having neutralizable groups, those polymers which are soluble in the neutralized form in a 50:50 water/ethanol solvent mixture (vol%:vol%) in an amount of more than 0.1 g/L, preferably more than 0.2 g/L, are preferred.

The polymers according to this invention are suitable for use as active ingredients in cosmetic preparations, whether as cosmetic preparations for use on the skin, such as liquid soaps, body lotions, shaving lotions, facial tonic, deodorants and other cosmetic lotions or especially hair care preparations, such as hair tonics, hair lotions, hair rinses, hair emulsions, tip fluids, neutralizers 0for permanent waves, hot oil treatment preparations, conditioners, hair setting lotions and hair sprays. Depending on the application, the hair care preparations may also be applied in the form of a spray, foam, gel, gel spray, lotion or mousse.

The mixtures according to this invention can be processed with the additives that are usually used in cosmetic preparations such as perfume oils, emulsifiers, preservatives, hair care substances such as panthenol, collagen, vitamins, protein hydrolysates, stabilizers, pH regulators, dyes, solvents, propellant gases and other conventional additives to yield gels, sprays, lotions or foams.

Examples

The following silicone surfactants Wacker B™ DMC 6031 and 6032 used in these examples are available from Wacker Chemie GmbH, Munich, and they have the following general structure:



where R = H, $CO-CH_3$

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The silicone surfactants Silwet ™ 7600, 7604 and 7605 are available from the company Witco Corporation, Greenwich, CT, USA and have the following general structure:

$$\begin{array}{c} Me_3SiO(Me_2SiO)_x(MeSiO)_ySiMe_3 \\ \quad\quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad\quad PE \end{array}$$

$$PE = -CH_2CH_2CH_2O(EO)_m(PO)_nZ$$

Z = hydrogen radical or alkyl radical

The silicone surfactants Dow Corning 190 Surfactant™ are available from Dow Corning Corporation, Midland, MI, USA.

Additional silicone derivatives (b) may also be synthesized by methods with which those skilled in the art are familiar, such as those described in European Patent 775717.

Examples 1 through 7

To a stirred recipient are added by drops 50 g feed stream 1 and 3.75 g feed stream 2. The mixture is then heated to 78 °Celsius. Next within 1.5 hours, the remainders of feed stream 1 and feed stream 2 are added by drops. This mixture is stirred for 2 more hours. Then feed stream 3 is added by drops within 15 minutes and stirred for another 3 hours at 78 °Celsius.

Example 1

Recipient: 175 g ethanol, 7.5 g Dow Corning 190™

Feed stream 1:	251 g tert-butyl acrylate, 86 g methacrylic acid, 37 g ethyl acrylate, 75 g ethanol
Feed stream 2:	2 g tert-butyl perpivalate 100 g ethanol
Feed steam 3:	1.5 g tert-butyl perpivalate, 57 g ethanol

Example 2

Recipient:	175 g ethanol, 18.75 g Dow Corning 190™
Feed stream 1:	251 g tert-butyl acrylate, 86 g methacrylic acid, 37 g ethyl acrylate, 75 g ethanol
Feed stream 2:	2 g tert-butyl perpivalate 100 g ethanol
Feed steam 3:	1.5 g tert-butyl perpivalate, 57 g ethanol

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Example 3

Recipient:	175 g ethanol, 37.5 g Dow Corning 190™
Feed stream 1:	251 g tert-butyl acrylate, 86 g methacrylic acid, 37 g ethyl acrylate, 75 g ethanol
Feed stream 2:	2 g tert-butyl perpivalate 100 g ethanol
Feed steam 3:	1.5 g tert-butyl perpivalate, 57 g ethanol

Example 4

Recipient:	175 g ethanol, 18.75 g Belsil DMC 6031™
Feed stream 1:	251 g tert-butyl acrylate, 86 g methacrylic acid, 37 g ethyl acrylate, 75 g ethanol
Feed stream 2:	2 g tert-butyl perpivalate 100 g ethanol
Feed steam 3:	1.5 g tert-butyl perpivalate, 57 g ethanol

Example 5

Recipient:	175 g ethanol, 37.5 g Belsil DMC 6031™
Feed stream 1:	279 g tert-butyl acrylate, 96 g methacrylic acid, 75 g ethanol
Feed stream 2:	2 g tert-butyl perpivalate 100 g ethanol
Feed steam 3:	1.5 g tert-butyl perpivalate, 57 g ethanol

Example 6

Recipient:	175 g ethanol, 37.5 g Belsil DMC 6032™
Feed stream 1:	300 g tert-butyl acrylate, 75 g methacrylic acid, 75 g ethanol
Feed stream 2:	2 g tert-butyl perpivalate 100 g ethanol
Feed steam 3:	1.5 g tert-butyl perpivalate, 57 g ethanol

Example 7

Recipient:	175 g ethanol
Feed stream 1:	251 g tert-butyl acrylate, 86 g methacrylic acid, 37 g ethyl acrylate, 75 g ethanol
Feed stream 2:	2 g tert-butyl perpivalate 100 g ethanol
Feed steam 3:	1.5 g tert-butyl perpivalate, 57 g ethanol

Example 8

After polymerization, the solution of the polymer from Example 7 is mixed with 10 percent by weight, based on the resulting polymer, of the silicon derivative Belsil DMC 6032™.

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Example 9

In a stirred apparatus 40 g Silwet ™ L 7604 and 180 g water were placed as the starting mixture. While stirring in a stream of nitrogen, the mixture was heated to 60 °Celsius, and feed stream 1 consisting of 240 g N-, 267 g 3-methyl-1-vinylimidazolium methyl sulfate solution (45 %) and 0.4 g mercaptoethanol and feed stream 2 consisting of 6 g 2,2'-azobis(2-amidinopropane) dihydrochloride and 70 mL water were added within 6 hours. Then the mixture was stirred for 2 more hours at 60 °Celsius and diluted with 200 g water, yielding a clear yellowish polymer solution with a solids content of 41.7% and a K value of 39 (1% in 0.5 M NaCl).

Example 10

In a stirred apparatus 40 g Silwet ™ L 7604 and 300 g water were placed as the starting mixture. While stirring in a stream of nitrogen, the mixture was heated to 65 °Celsius, and feed stream 1 consisting of 220 g N- and 333 g 3-methyl-1-vinylimidazolium chloride solution (60 %) and feed stream 2 consisting of 6 g 2,2'-azobis(2-amidinopropane) dihydrochloride and 70 mL water were added within 6 hours. Then the mixture was stirred for 2 more hours and then diluted with 100 g water, yielding a clear yellowish polymer solution with a solids content of 43.0 % and a K value of 44 (1 % in 0.5 M NaCl).

Example 11

In a stirred apparatus 24 g Silwet ™ L 7604 and 200 g water were placed as the starting mixture. While stirring in a stream of nitrogen, the mixture was heated to 65 °Celsius, and feed stream 1 consisting of 160 g N-, 80 g methacryloxyethyl-N-dimethyl-N-ethylammonium ethyl sulfate and 300 g water and feed stream 2 consisting of 1.3 g 2,2'-azobis(2-amidinopropane) dihydrochloride and 100 g water was added within 6 hours. Then the mixture was stirred for 2 more hours and diluted with 300 g water, yielding a clear yellowish polymer solution with a solids content of 22.4 % and a K value of 85 (1 % in 0.5 M NaCl).

Examples 12 and 13

In a mixture of 1.4 mercaptoethanol, 5.8 g of a polyacrylic acid (available under the name Sokalan PA 110 S from BASF AG), 306 g N-tert-butylacrylamide, 234 g ethyl acrylate, 60 g acrylic acid and 60 g of a dimethicone copolyol were suspended. After heating to 75 °Celsius, 1.2 g tert-butyl peroctoate was added to the resulting suspension. One additional gram of tert-butyl peroctoate was added after 30 minutes and again after 45 minutes. After the following times, more initiator was added: 1 hour: 1 g at 80 °Celsius; 1.5 hours: 1 g; 2 hours: 1 g at 90

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°Celsius; 3 hours: 2.7 g; after 4.5 and 6 h: 1 g each. Then it was postpolymerized for 1 hour.

The following dimethicone polyols were used:

Example 12: Wacker Belsil DMC 6031

Example 13a: Wacker Belsil DMC 6032

Example 13b: Witco Silwet® L-7500

Example 14 (Comparative Example)

In a mixture of 1.4 g mercaptoethanol, 5.8 g of a polyacrylic acid (available under the name Sokalan PA 110 S from BASF AG), 306 g N-tert-butylacrylamide, 234 g ethyl acrylate and 60 g acrylic acid were suspended. To the resulting suspension were added after heating to 75 °Celsius: 1.2 g tert-butyl peroctoate. After 30 and 45 minutes, 1 additional gram of tert-butyl peroctoate was added each time. Additional initiator was added after the following times: 1 hour: 1 g at 80 °Celsius ; 1.5 hours: 1 g; 2 hours: 1 g at 90 °Celsius; 3 hours: 2.7 g; after 4.5 and 6 hours: 1 g each. Then postpolymerization was performed for 1 hour.

Example 15

A mixture of 744 g water, 0.25 g sodium lauryl sulfate and 70 g feed stream 1 was heated to 40 °Celsius. Then 16 g of a 7% aqueous sodium persulfate solution was added. Then the mixture was heated to 80 °Celsius and feed stream 1 was added over a period of 2 hours. Then 178 g water was added and postpolymerization was performed at 80 °Celsius for 2 hours.

Feed stream 1:	300 g water
	2 g sodium lauryl sulfate
	15.7 g silicone copolyol (Silwet L7605)
	470 g tert-butyl acrylate
	70 g ethyl acrylate
	161 g methacrylic acid
	3 g ethyl hexyl thioglycolate

Example 16

A mixture of 744 g water, 0.25 g sodium lauryl sulfate and 70 g feed stream 1 was heated to 40 °Celsius. Then 16 g of a 7 % aqueous sodium persulfate solution was added. Next, the mixture was heated to 80

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°Celsius and feed stream 1 was added over a period of 2 hours. Then 178 g water was added and postpolymerization was performed at 80 °Celsius for 2 hours.

Feed stream 1:
- 300 g water
- 2 g sodium lauryl sulfate
- 15.7 g PEO (20) sorbitan monooleate
- 422 g tert-butyl acrylate
- 63 g ethyl acrylate
- 145 g methacrylic acid
- 3 g ethyl hexyl thioglycolate
- 70 g silicone copolyol (Silwet™ L7605)

Example 17

A mixture of 744 g water, 0.25 g sodium lauryl sulfate and 70 g feed stream 1 was heated to 40 °Celsius. Then 16 g of a 7% aqueous sodium persulfate solution was added. The mixture was next heated to 80 °Celsius and feed stream 1 was added over a period of 2 hours. Then 178 g water was added and postpolymerization was performed at 80 °Celsius for 2 hours.

Feed stream 1:
- 300 g water
- 2 g sodium lauryl sulfate
- 15.7 g silicone copolyol (Silwet L7600)
- 470 g tert-butyl acrylate
- 70 g ethyl acrylate
- 161 g methacrylic acid
- 3 g ethyl hexyl thioglycolate

Example 18

A mixture of 744 g water, 0.25 g sodium lauryl sulfate and 70 g feed stream 1 was heated to 40 °Celsius. Then 16 g of a 7% aqueous sodium persulfate solution was added. The mixture was then heated to 80 °Celsius and feed stream 1 was added over a period of 2 hours. Then 178 g water was added and postpolymerization was performed for 2 hours at 80 °Celsius.

Feed stream 1:
- 300 g water
- 2 g sodium lauryl sulfate
- 15.7 g PEO (20) sorbitan monooleate
- 422 g tert-butyl acrylate
- 63 g ethyl acrylate
- 145 g methacrylic acid
- 3 g ethyl hexyl thioglycolate

70 g silicone copolyol (Silwet ™ L7605)

Example 19

A mixture of 744 g water, 0.25 g sodium lauryl sulfate and 70 g feed stream 1 was heated to 40 °Celsius. Then 16 g of a 7 % aqueous sodium persulfate solution was added. Next the mixture was heated to 80 °Celsius and feed stream 1 was added over a period of 2 hours. Then 178 g water was added and postpolymerization was performed at 80 °Celsius for 2 hours.

Feed stream 1:
300 g water
2 g sodium lauryl sulfate
15.7 g PEO (20) sorbitan monooleate (Tween 80)
422 g tert-butyl acrylate
63 g ethyl acrylate
145 g methacrylic acid
3 g ethyl hexyl thioglycolate
70 g silicone copolyol (Silwet ™ L7600)

Example 20 (Comparative Example)

A mixture of 744 g water, 0.25 g sodium lauryl sulfate and 70 g feed stream 1 was heated to 40 °Celsius. Then 16 g of a 7 % aqueous sodium persulfate solution was added. The mixture was next heated to 80 °Celsius and feed stream 1 was added over a period of 2 hours. Then 178 g water was added, and postpolymerization was performed for 2 hours at 80 °Celsius.

Feed stream 1:
300 g water
2 g sodium lauryl sulfate
15.7 g PEO (20) sorbitan monooleate (Tween 80)
470 g tert-butyl acrylate
70 g ethyl acrylate
161 g methacrylic acid
3 g ethyl hexyl thioglycolate

Example 21

A mixture of 100 g vinylcaprolactam, 100 g ethanol, 100 g dimethicone copolyol (Wacker Belsil ™ DMC 6031) and 0.75 g tert-butyl perpivalate was heated to 70 °Celsius in a closed capsule purged with nitrogen. Then feed stream 1 was added within 3 hours and feed stream 2 was added within 4 hours. After the end of addition of feed stream 1, postpolymerization was performed for 1 hour. Then feed stream 3 was added and the mixture was heated to 130 °Celsius under pressure and then

postpolymerized for 10 hours at 130 °Celsius and finally cooled.

Feed stream 1:	800 g Vinylcaprolactam
	347 g ethanol
Feed stream 2:	1.5 g t-butyl perpivalate
	100 g ethanol
Feed stream 3:	5 g di-tert-butyl peroxide
	187 g ethanol

Example 22

A mixture of 100 g vinylcaprolactam, 100 g ethanol, 100 g dimethicone copolyol (Wacker Belsil™ DMC 6032) and 0.75 g tert-butyl perpivalate was heated to 70 °Celsius in a closed capsule which was purged with nitrogen. Feed stream 1 was then added within 3 hours and feed stream 2 within 4 hours. After the end of addition of feed stream 1, postpolymerization was performed for 1 hour. Then feed stream 3 was added and the mixture was heated to 130 °Celsius under pressure and then postpolymerized for 10 hours at 130 °Celsius and then cooled.

Feed stream 1:	800 g vinylcaprolactam
	347 g ethanol
Feed stream 2:	1.5 g t-butyl perpivalate
	100 g ethanol
Feed stream 3:	5 g di-tert-butyl peroxide
	187 g ethanol

Example 23 (Comparative Example)

A mixture of 100 g vinylcaprolactam, 100 g ethanol and 0.75 g tert-butyl perpivalate was heated to 70 °Celsius in a closed capsule purged with nitrogen. Then feed stream 1 was added within 3 hours and feed stream 2 was added within 4 hours. After adding feed stream 1, postpolymerization was performed for 1 hour. Then feed stream 3 was added and the mixture was heated to 130 °Celsius under pressure and then postpolymerized for 10 hours at 130 °Celsius and then cooled.

Feed stream 1:	800 g Vinylcaprolactam
	347 g ethanol
Feed stream 2:	1.5 g t-butyl perpivalate
	100 g ethanol
Feed stream 3:	5 g di-tert-butyl peroxide
	187 g ethanol

Example 24

The polymer solution from Example 23 was mixed with 10 percent by weight of a silicone surfactant (Wacker Belsil™ DMC 6032) after polymerization.

Films of the polymer from the examples were prepared by applying the solutions or dispersions of the polymers to glass plates with a doctor blade. The transparency of these films and the surface roughness and frictional behavior of the polymer films were determined (see Table 1).

It was found that all the films according to this invention were transparent and had an especially smooth surface with low frictional resistance.

Films from Comparative Example 7 are also transparent but they have a rougher surface and especially a much higher frictional resistance. The same poor frictional behavior was also found for films from Examples 8, 14, 20, 23 and 24. Films produced from blends of Examples 8 and 24 by a similar method were extremely sticky. These films were very soft and were therefore unsuitable for use as film-forming agents.

Tests of polymers 1 through 24 to determine their suitability as hair care products yielded similar results (Table 1). The tests were performed by spraying tresses of hair with a defined quantity of a standard formulation of the polymer (2 percent by weight polymer, 40 % dimethyl ether, 58 % ethanol). After drying the tresses of hair, the combability and feel were evaluated on these strands of hair. The polymer products produced according to this invention in the presence of silicone surfactants yielded a much better feel of the strands of hair treated with them than the strands of hair treated with the polymers from Comparative Examples 7, 14, 20, 23.

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Table 1

Example	Smoothness of the film	Transparency	Combability	Feel
1	0	+	0	0
2	+	+	+	-
3	+	+	+	0
4	+	+	+	0
5	++	+	++	++
6	+	+	++	0
7	—	+	-	—
8	—	0	-*	-*
12	+	+	++	++
13a	+	+	++	+
13b	+	+	++	+
14	-	+	++	0
21	+	+	+	+
22	+	+	++	+
23	-	+	0	-
24	—	-	-*	-+

* because of the extreme stickiness, we did not do a test on the hair strands

The entries in the table have the following meaning:

++ = very good performance
+ = good performance
0 = satisfactory performance
– = not satisfactory
-- = insufficient

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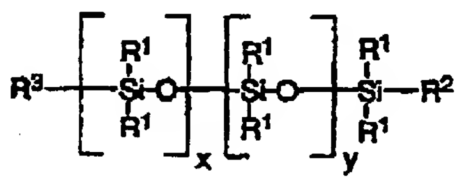
Patent Claims

1. Use of polymers that are water-soluble or water-dispersible or, in the case when they consist of monomers with neutralizable groups, they are water-soluble or water-dispersible in a neutralized form and are accessible by radical polymerization of
   (a) ethylenically unsaturated monomers in the presence of
   (b) silicone derivatives containing polyalkylene oxide
   for cosmetic formulations.

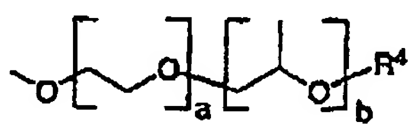
2. Use according to Claim 1, characterized in that the silicone derivatives (b) containing polyalkylene oxide are those of formula 1



(I)

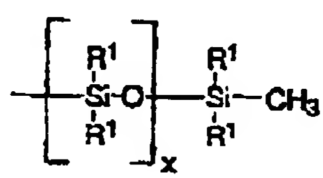
where:

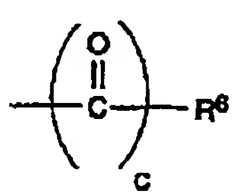
R^2 = CH_3 oder



R^3 = CH_3 oder R^2

R^4 = H, CH_3,





[Translator's note: "oder" = "or"]

R^6 is an organic group consisting of 1 to 40 carbon atoms which may contain amino groups, carboxylic acid groups or

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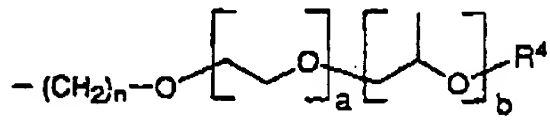
sulfonate groups, or in the case when c = 0, it may also be the anion of an inorganic acid,

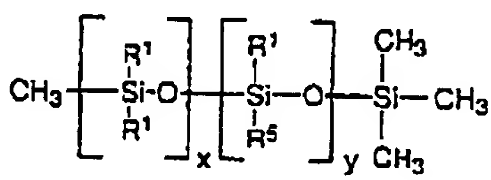
and where the R^1 groups may be identical or different and are selected either from the group of aliphatic hydrocarbons with 1 to 20 carbon atoms, cyclic aliphatic hydrocarbon groups with 3 to 20 carbon atoms, or they are of an aromatic nature or the same as R^5 where:

$R^5 =$ 

with the provision that at least one of the R^1, R^2 or R^3 groups is a group containing polyalkylene oxide according to the definition given above,

and n is an integer from 1 to 6,
x and y are integers such that the molecular weight of the polysiloxane block is between 300 and 30,000,
a and b are integers between 0 and 50, with the provision that the sum of a + b is greater than 0, and c is 0 or 1.

3. Use according to Claim 2, characterized in that formula I has the following meaning:



4. Use according to Claim 1, characterized in that the quantity ratios are

(a) 50 to 99.9 percent by weight and
(b) 0.1 to 50 percent by weight.

5. Use according to Claims 1 through 4 as a hair care product.

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(54) Title: USE OF POLYMERS CONTAINING POLYSILOXANE FOR COSMETIC FORMULATIONS

(57) **Abstract**

The invention relates to a method for producing polymers which are water-soluble or water-dispersible or which, if they consist of monomers with neutralizable radicals, are water-soluble or water-dispersible in the neutralized form, by radically polymerizing a) ethylenically unsaturated monomers in the presence of b) silicone derivatives containing polyalkyleneoxide.

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